ANALYSIS AND ORIGIN OF POINT DEFECTS IN SILICON AFTER LIQUID PHASE TRANSIENT ANNEALING

A. Mesli, J. Muller, P. Siffert

JOURNAL DE PHYSIQUE
Colloque C5, supplément au n°10, Tome 44, octobre 1983

ANALYSIS AND ORIGIN OF POINT DEFECTS IN SILICON AFTER LIQUID PHASE TRANSIENT ANNEALING

A. Mesli, J.C. Muller and P. Siffert

Centre de Recherches Nucléaires, Laboratoire PHASE, 67037 Strasbourg Cedex, France

Résumé - Nous présentons une revue des travaux consacrés à l'étude des défauts ponctuels observés par des mesures électriques sur du silicium irradié par laser pulsé. Dans le cas du silicium amorphisé par implantation, il est montré que les effets de queue de distribution sont responsables de la majorité des défauts résiduels observés. Par contre, des analyses effectuées sur du silicium légèrement endommagé, ont montré qu'il est difficile de recuire certains défauts ponctuels quand la durée d'impulsion diminue. Enfin, l'étude des défauts ponctuels créés par le processus laser dans le silicium vierge met en évidence, essentiellement, des états donneurs. Ces derniers introduisent un effet de compensation des matériaux de type P.

Abstract - Works devoted to the study of point defects in pulsed laser annealed silicon are reviewed by means of electrical characterization. Tailing effects of the implanted distribution are responsible for the observed residual defects in the case of a layer amorphized by ion implantation. However, difficulty in annealing some kinds of point defects by reducing the duration of laser pulse have been shown using slightly disordered silicon. Finally, in the case of irradiated virgin silicon, a high level of point defects are created, which are essentially donor levels that introduce a compensating effect in P-type silicon.

INTRODUCTION

The use of high power laser annealing has been considered with much interest over the past few years since it offers certain advantages compared to the furnace annealing or the continuous laser process. The three major properties of the pulsed laser annealing can be summarized as follow :

First, spatially localized annealing offers advantages in microelectronics technology. For example, it can be used to anneal the implanted microstructures without degrading minority carrier lifetime in the bulk.

Secondly, the process offers a high efficiency for the introduction of the implant dopant into substitutional positions /1, 3/ except for the implanted impurity that exhibits a low-equilibrium solubility in the lattice that precipitates upon annealing /4/.

Thirdly pulsed annealing seems to produce good quality recrystallization of the implanted region. This topic has been largely analyzed using techniques like RBS and TEM /5/. However, more sensitive methods including photoluminescence IR absorption, EPR analysis, and electrical measurements such as DLTS have shown that defects subsists in the annealed layer or are created by the laser process. The electrical role of these defects is critical and can partially reduce the potential advantages brought to semiconductor technology by localized surface melting.

In this paper we will review the electrical properties of pulsed laser irradiation of silicon :

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:1983543

- For P-N junction prepared by ion implantation at a doping level assuming the amorphization of the front layer.
- For slightly disordered layers by means of low dose light ion implantation or light particle irradiation (e^-, n, γ, ...).
- For Schottky structures realized on virgin material processed by pulsed laser.

I - LASER PULSE ANNEALING OF AMORPHIZED LAYERS BY ION BOMBARDMENT

I.1 - EXISTENCE OF A LASER POWER THRESHOLD FOR MINIMUM DEFECTS

Processing by pulse annealing of ion implanted layers must ensure a high electrical activation of the introduced dopant and as well as a minimum residual defect level. The laser power which satisfies both of these conditions is called the "threshold energy to have a minimum defect density" lower power leaves a high concentration of point defects near the junction, while higher power may introduce laser process related defects.

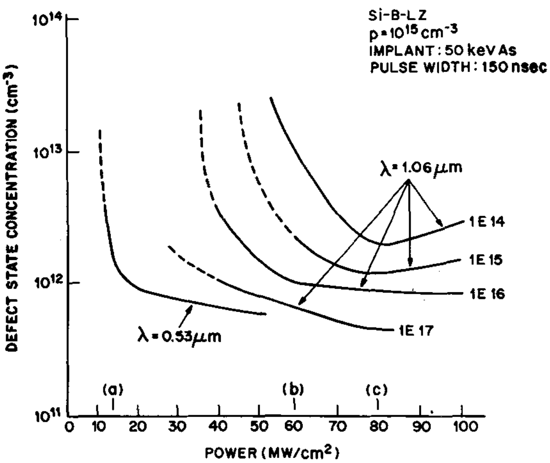


Fig. 1 - Total defect state concentration observed by capacitance transient spectroscopy in arsenic implanted, laser processed n^+p junctions. Low defect threshold conditions are denoted as (a) λ = 0.53 μm light for all implant doses: (b) λ = 1.06 μm light. As (50 keV) = 10^{16} cm^{-2}; (c) λ = 1.06 μm. As (50 keV) = 10^{14} cm^{-2}. /6/

Kimerling and al. /6/ have shown (Figure 1) that the laser power threshold for minimum defects is independent on the type of pulsed laser used. In the case of YAG (1.06 μm) they have shown a decreasing minimum point defect with increasing dopant implanted dose due to the enhanced free carriers coupling of the light. On the other hand for the doubled frequency Nd-YAG in which band to band absorption occurs, the limit is lower and independent of dose.

These results are similar to those obtained for a ruby laser (Figure 2)

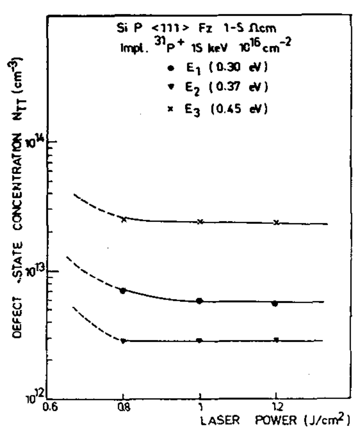


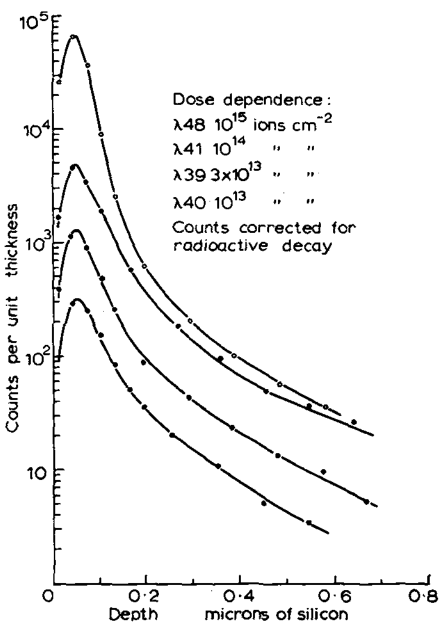
Fig. 2 - Total defect state concentration of the three electron traps after various ruby laser pulse energies. /7/.

I.2 - ORIGIN OF THE DEFECT ANNEALING LIMIT

If there is general agreement /6 - 13/ that for device preparation the laser processing must melt both the implanted dopant distribution as well as any defect buried beyond the front amorphized layer in a region called the "Implantation tail", it remains important to determine if laser annealing conditions can be found to assure or not the condition <<depth of melting equals the depth of implantation damage>> /6, 8/.

Two concepts can be postulated. First : a) melt depth never equals the implant damage depth and second : b) the molten layer covers the damage zone and at higher laser power the laser related defects are dominant.

a) Concept of implant residual defects



According to this concept, the defect annealing limit is correlated with residual defects buried too deeply to be touched by the melt depth, so that higher laser energies, but still lower than the limit of visible degradation of the surface, can not guarantee the condition "depth of melting equals the depth of implantation damage".

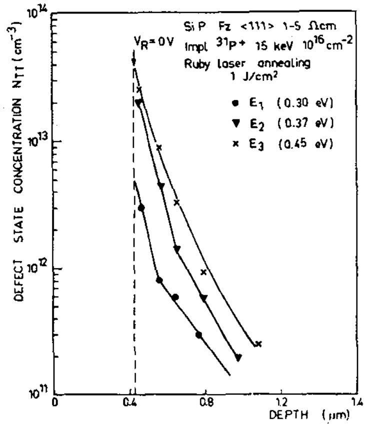
Blood and al. /14/ have shown that the tailing effect is important even more if the implantation is performed at room temperature and off-axis as illustrated on Figure 3. The tail has an exponential slope which results in a great penetration (over 1 μm) for concentration four or five orders of magnitude lower than the maximum.

Fig. 3 - The dose dependence of profiles of 40 keV ^{32}P ions implanted into misaligned <110> crystals at room temperature. /14/.

The tailing effect is due to a pure diffusion mechanism /15/ which can be enhanced by the presence of point defects, by the crystal temperature or by channeling phenomena if the implantation is performed on-axis.

In the latter case the recrystallization will be initiated in a region containing defects and the quality of regrowth will be influenced by the number of residual traps at the point of regrowth.

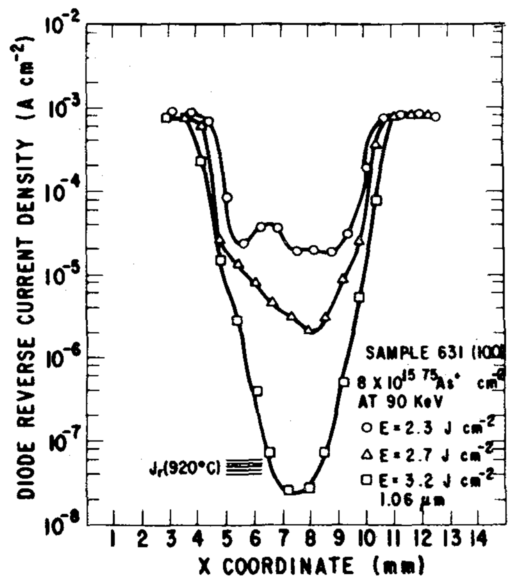
In agreement with this idea some authors /7, 10, 11/ have shown that in the case of an implantation at dose sufficient for the amorphization of the first layer, many traps are present with an extension deeper than the implanted range and deeper than the melt depth. However, it was found /7, 11/ that the defect distribution decreases with an exponential slope as illustrated in Figure 4. Moreover Mesli /16/ has reported that all these observed defects are dependent on implantation parameters like energy, ion flux, temperature and orientation of the substrate.



Skolnick et al. /12/ have studied by photoluminescence the defects in silicon amorphized by silicon ions. After ruby laser annealing, they found a photoluminescent line not removed even at an energy of 2.5 J/cm². They conclude that this defect is produced during the implantation in the region of lower damage beyond the amorphous region in the channeling tail of the implant even if the implantation is performed off-axis.

Fig. 4 - Depth profile of the three defects after 1 J/cm² ruby laser annealing. The limit of measurements at zero bias voltage is given by the dashed line. /7/.

In the same way Brower and Peercy /13/ nave found by EPR measurements and ruby laser annealing of phosphorus implanted in silicon simultaneously amorphized by silicon ions that the efficiency of the laser annealing increases when the energy of the incident ions is reduced.



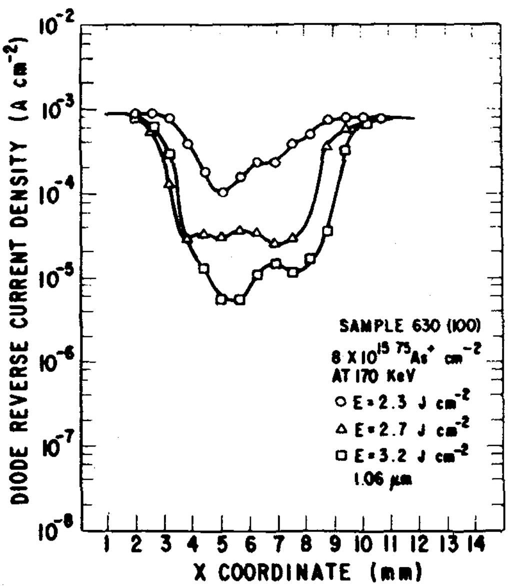


Fig. 5 (a) - Diode leakage current density for samples implanted at 90 keV with an As fluence of 8 x 10^{15} cm^{-2}. The laser annealing energy density was 2.3 J-cm^{-2} (O), 2.7 J-cm^{-2} (Δ), and 3.2 J-cm^{-2} (□), respectively. The data for a thermally-annealed diode are shown for comparison (T = 920° C). /11/.

Fig. 5 (b) - Diode leakage current density for samples implanted at 170 keV. Other parameters are the same as those in (a). /11/.

This is also confirmed by the diode leakage current measurements performed by Wang et al. /11/ (Fig. 5 a and b). Complementary carrier collection efficiency (coming from EBIC data) suggest that the defects distribution has a long tail with a significant defect concentration.

By double X-ray diffractometry Servidori et al. /17/ have shown that the observed disorder which decreases the lattice parameters of silicon extend to depths much greather than the amorphized region.

To confirm that the observed defects are due to some "long tail". Mesli et al. /7/ have removed the defects in the lightly damaged region by a low temperature annealing (400° C) not sufficient to change, the absorption condition in the surface amorphized layer so that the melt depth will not be changed.

In this case DLTS spectra have shown that defects are no longer present (Fig. 6) after laser irradiation in the space charge region of the junction. It is also to be noted that the laser energy (1 J/cm^2) is too low to create laser related defects in this deep region.

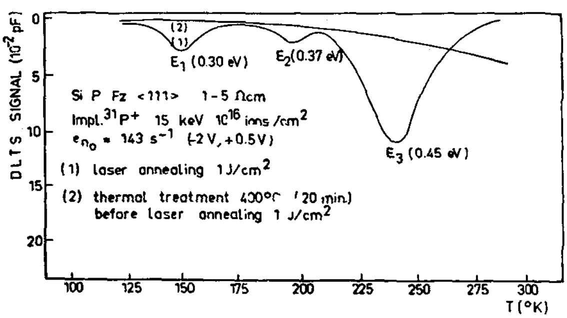


Fig. 6 - DLTS signal when a conventional thermal annealing is performed before the laser treatment. /7/.

b) Laser introduced defects after high laser power exposure

This concept is illustrated in Figure 1 by the fact that an increase of the concentration of point defects is observed for laser energies over the minimum defect threshold. Several possible sources of defect introduction during laser treatment can be enumerated : surface contamination, ambiant processing in air, crystal regrowth velocity, high temperature gradients, quenching, etc ... The most important question is to determine the importance of laser related defects present deep in the crystal in the charge space region of the junction.

For some authors like Skolnick et al. /12/ the melting and rapid recrystallization of crystalline silicon do not produce a significant number of radiative point defects, while no photoluminescent line (or very weak lines) are observed for ruby laser annealing of unimplanted samples with energies ranging from 0 to 2.5 J/cm^2. However, a line has been found to be produced by solid phase annealing of the ion implanted damage in the channeling tail beyond the amorphized region. This line has never been observed after laser processing of implanted samples and is not present after the ion implantation alone so that laser heating is therefore necessary to produce this level. Thus laser treatment can reveal and enhance some defects.

While electrical studies (sensitive only in the space charge region) of devices realized by ion implantation and subsequent laser annealing typically reveal implantation defects lying beyond the doped region, the laser processing defects are best studied by observing changes induced in an undamaged surface layer in Schottky barrier structures. This will be discussed in Paragraph III.

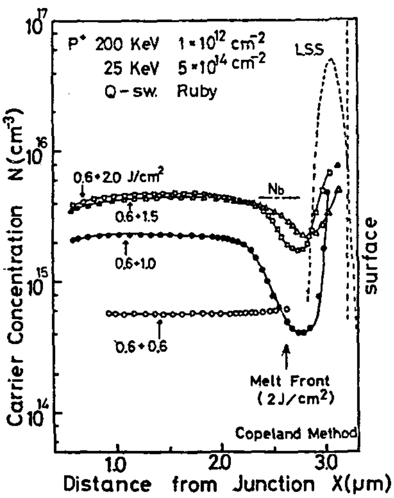
I.3 - ROLE OF THE FRONT AMORPHIZED LAYER

The question here is if a front amorphized layer can act as a mash for good annealing of deep defects, or in contrary, can be better as the absorption of light and melt depth is greather.

a) The amorphized layer as a mash

Brower /13/ has shown by EPR analysis of the paramagnetic lattice damage recovery that the recrystallization of low dose phosphorus implantation is better if the front layer is not amorphized.

Moreover the argument that the amorphized layer can play a role of barrier has been used by Sasaki et al. /18/ in the discussion of the two kinetic models "melting" or "plasma" annealing. This group has performed double implantation of ^{31}P, low dose to dope and high dose to form an amorphized front layer. In agreement with precedent works /6, 7/, they found traps underneath the amorphized layer.



By using double laser irradiation (Figure 7) where the first removes the amorphized layer and the second anneals the deep defects, they have a better annealing that using a single laser shoot through the amorphized layer.

These authors suggest that after the first laser pulse the absorption length of surface region becomes larger so that the second laser beam can be transmitted deeper into the crystal and can anneal the deep lying defects.

Fig. 7 - Carrier profiles of the double irradiated samples /18/

In classical thermal model carrier recovery may have occured easier in the sample which have the surface amorphized layer, in this case melt depth is larger than in crystalline silicon for the same energy as predicted by the models /19/. As this assumption contradictes the previous results, the authors conclude that the process of carrier recovery in the deep region is not melting and recrystallization but is related to the deep penetration of light in the crystal so that it is the plasma mechanism that occurs.

However, it must be remembered that annealing of some point defects can occur by solid phase epitaxy in the hot region adjacent to the melt as will seen in the section II.

b) The positive role of the amorphized layer

Nakashima et al. /20/ reported by photoluminescence of laser annealing of phosphorus implanted layers that the regrowth is better for high doses of $^{31}P^{+}$ than for low doses, due to a higher absorption region which enhances the temperature rise.

It has been also shown by Young /21/ that the recrystallization velocity V can play a role. The decrease of V has been correlated to better electrical characteristics of the junction (by measurements of solar cell parameters under illumination). Experimentally the regrowth velocity has been diminished by increasing the temperature of the substrate during the laser annealing, but the suggest that the quality of the regrowth layer is dependent on V cannot be confirmed by this experiment while the melt-depth increases so that the concentration sprawl out and the junction is deeper. For the first concept, in which the recrystallization is initiated in the exponential tail of the implanted damage, the quality of regrowth will be better if we start in a more deeper region /7/.

I.4 - ASSIGNMENT AND ANNEALING OF POINT DEFECTS

The first tentative assignment of the levels was made by Kimerling et al. /6/ and Wang et al. /11/. They tended to separate those observed in ion implantation from those present in irradiated bare silicon. Some of them are clearly related to residual ion damage like E (0.18 eV) which is observed also after 1 MeV electron bombardment, this can then be assigned to $|V - O|$ defects also reported by /7/ with an annealing temperature of 400° C. This is different from E (0.19 eV) reported by Kimerling /6/ on bare liquid phase processed silicon that disappears only at 550°C.

In the range of 0.27 - 0.37 eV, electron traps are found correlated to defects which increase in concentration by increasing the mass particules. They are assigned to multicomplex defects E (0.27 eV) or multivacancies centers.

A similar assignment is given for the photoluminescent line and for defects observed by X-ray diffractometry /17/.

The H (0.36 eV) has been assigned to carbon related defects /8/ $|V - C_i - O|$ which disappears at 400 - 500° C.

Deeper defects E (0.45 eV - 0.53 eV) have been associated with divacancy and pentavacancy /7/ with a higher annealing temperature.

The most important point is that all these defects disappear at least for the most complex defects (V^5), at a temperature around 600° C so that a post laser treatment performed at this temperature is necessary and sufficient to attain good junction characteristics as reported by /22, 23/.

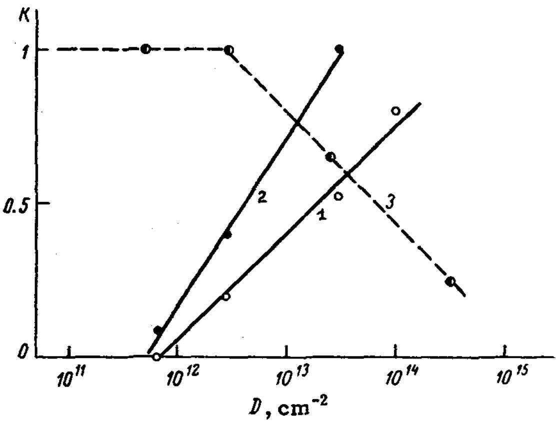
II - PULSED LASER ANNEALING IN SLIGHTLY DISORDERED SILICON

The principal conclusion of the foregoing section is that pulsed laser annealing of highly doped layers by ion implantation is much more efficient in the amorphized region than in the slightly disordered adjacent tail region.

In this section we will discuss more precisely the annealing of slightly disordered crystalline silicon by means of low dose ion implantation or light particules irradiation (e^-, n, γ ...).

Much less attention has been devoted to this situation in which the mechanism of annealing of each individual point defect can be studied as opposed to the overall annealing described in the first section in which amorphization takes place.

When light ions are implanted into silicon at small doses that maintain the crystalline aspect of the target, some authors /24, 25/ have observed a electrical compensating effect of the implanted dopant level after pulsed laser annealing; phenomenon related to the presence of point defects and their complexes with high concentrations in the annealed layer. This has been confirmed by measurement of the variation of the bulk mobility that is a function of the number of the scattering centers /25/. This compensation influences the "impurity utilization coefficient" of the implanted dopant. Fig. 8 shows the variation of this coefficient versus dose of the phosphorus implanted into N-type silicon for differents ruby laser energies. In the case of thermal annealing (700° C, 15 mn, dashed curve) we notice the well know decline in the utilization coefficient with implantation dose due to the dopant precipitation process.



However, for pulsed laser annealing, the coefficient decreases with decreasing dose, and the efficiency of the doping increases with laser energy. This shows that at low dose implantation, it is difficult to have a total activity of the dopant even if the silicon is only slightly disordered.

Fig. 8 - Dependence of the impurity utilization coefficient on the phosphorus ion dose after laser (1, 2) and thermal (3) annealing. Laser pulse energy (J/cm^2) : 1) 1.6; 2) 2.5. Thermal annealing at 700° C for 15 min. /25/.

It seems that it is more difficult to anneal completly the residual damage even with high laser power.

These observations are in contrast to classical annealing kinetics when most residual defects like P - V complex (E center) or V - O (A center) and vacancy complexes anneal out in the range of 150 - 500° C.

In order to understand the pulsed laser annealing kinetics of point defects, a uniform formation of damage by bombardment with light particules associated with analysis techniques such as DLTS or IR absorption would appear to be usefull. These kinds of methods offer the possibility of controlling the nature of point defects and of following their concentration and profiles in the bulk with the parameters of the annealing process.

Using these techniques, Kachurin et al. /26/ and Kimerling et al. /6/ have shown that, after fast electron irradiation of silicon and Q switched ruby or Nd YAG laser annealing,the various types of point defects created are not all removed at the same time. Certains defects need higher power as illustrated in Figures 9 and 10.

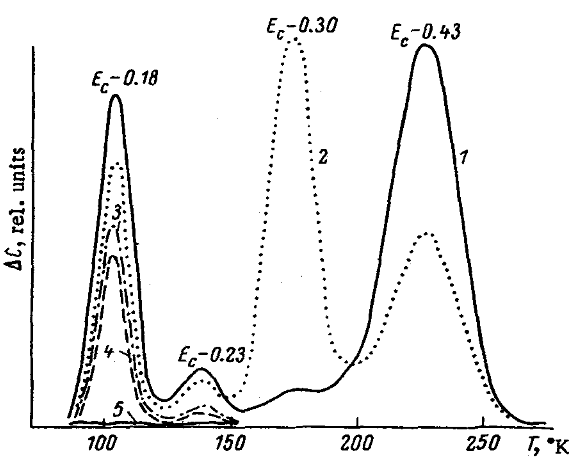


Fig. 9 - Peak amplitude variations in DLTS spectra of radiation defects formed by electron irradiation, after the action of laser pulses with various energies. Laser pulse energy (J/cm^2) : 1) original. 2) 0.4. 3) 1.1. 4) 1.4. 5) 1.8. Spectrum recorded in 3msec time "window" (t_1 = 1 msec. t_2 = 4 msec). Ionization energy of centers in electron volts. /26/.

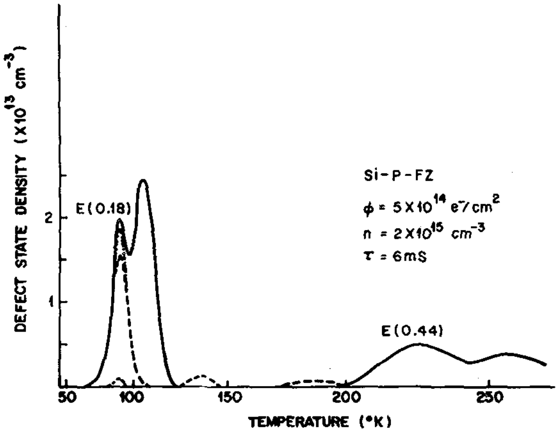
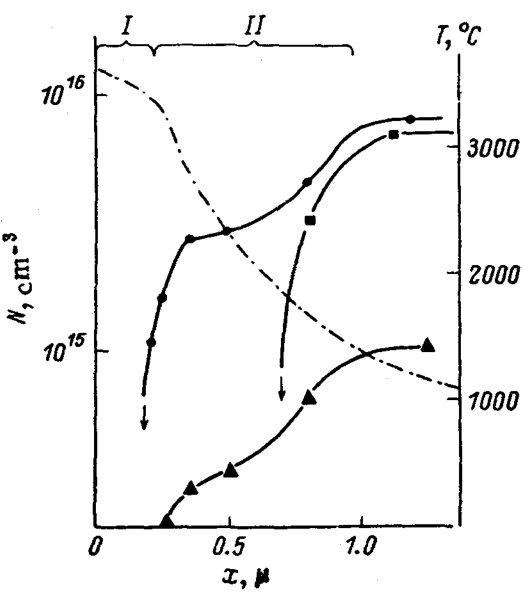


Fig. 10 - Defect state spectrum of 1-MeV electron irradiated, phosphorus doped, float-zoned silicon. ϕ = bombardment dose. τ = defect state emission time constant at temperature of peak maximum. Solid line : as-bombarded and Q-switch laser anneal: dashed curves : 1s. 10s. 30s cw laser anneal, consecutively. λ (laser) = 1.06 µm. /6/.

In Fig. 9, it is seen that the E center and level at E_c - 0.30 eV disappear when the pulse energy is $E \leq 1$ J/cm^2 for the ruby laser. However, the A center and the divacancy needs higher energies ($E \geq 1.5$ J/cm^2). The same authors have measured the radiation defect concentration as functions of depth for a pulse energy of 2.5 J/cm^2.

The results reported in Fig. 11 show that, for a sufficiently large pulse energy, the radiation defects disappear only from a thinner layer (0.2 - 0.3 µm) where the temperature exceeds that needed to melt the surface.



In excess of this depth, the annealing kinetics is specific to each defect. These observations, agree with what was said above about the difficulties in annealing the tail part of the point defect distribution since they are situated in a region adjacent to the melt depth.

To explain this result we must consider the duration of annealing which plays an important role.

Fig. 11 - Dependence of the radiation defect concentration on the depth for laser pulse energy 2.5 J/cm^2. Chain curves : calculated maximum temperature profile. I) Melting region. II) Superheated region. /26/.

In the classical model of the thermal annealing kinetics, the temperature T and the annealing time t are related by the following expressions :

$$N_{TT} = N_{To} \exp - t/\tau \qquad (1)$$

where N_{TT} is the concentration of point defects remaining after the laser process, N_{To} is their initial concentration and τ the rate of defect annealing. This later parameter depends on the temperature and activation energy U of the process.

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp - \frac{U}{KT} \quad (2) \quad (\frac{1}{\tau_0} \text{ is constant})$$

Using first order kinetics and the data published /27, 29/, and provided that extrapolation to short time is justified, the removal temperature of V - P, V - V and V - O centers are given in Fig. 12.

In this model, we assume that laser irradiation does not itself create point defects in a concentration comparable to that produced by bombardment or implantation at low doses, and that the annealed defects do not reform to produce new centers.

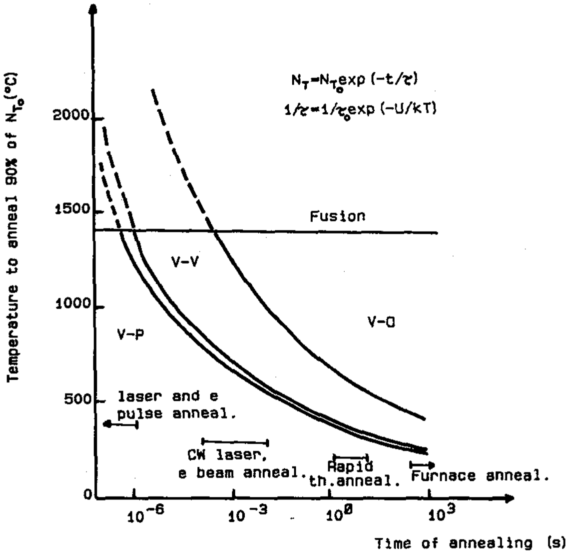


Fig. 12 - Annealing kinetics extrapolated to the short times.

Fig. 12 shows that in the classical annealing region the temperature needed to anneal points defects is slightly greather than that given in the literature /27, 29/. This is due to the ratio $N_{To} / N_{TT} = 10$ considered in our calculation. The temperature needed to anneal 90% of the point defects increases when the heating time is reduced, so that a temperature above the melting condition seems to be necessary to remove the V - O association for annealing times less than 10^{-3} sec. This is in agreement with the results reported by Kachurin et al. in Fig. 9, since this association is only removed in the liquid phase extension.

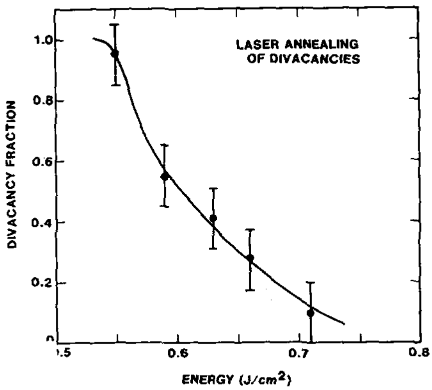
Elsewhere for pulse times used (20 - 50 ns), all classical thermal models indicate that the melting time is a few hundred nanoseconds and the total heating time is one ot two orders of magnitude greater. This ensure the annealing of V - P and V - V centers in the molten region of course, but also in the heated region adjacent to the melted zone where the temperature is sufficiently high to anneal within the duration of the process. Whereas this time is too short for any recovery of the V - O association in a region deeper than the melt, this explains the abrupt variation seen by Kachurin /26/ for this level at the boundary of the melt front.

The possibility of annealing some kinds of point defects, like the P - V and V - V associations, in the hot region near the molten layer can explain (in terms of the thermal model) the results of Sasaki /18/. The use of a double laser irradiation multiplies by two the total duration of the annealing.

Stein /30/ has studied the divacancy annealing in boron implanted silicon at a dose of 10^{14} cm^{-2}. He finds also that the V - V annealing begins at laser energies lower,that those expected for melting in crystalline silicon as reported in Fig. 13. However, for the implantation dose used, the damage can enhance photon absorption in the implanted layer and induce a decrease of the thermal conductivity so that the melt temperature is achieved at a lower laser energy that is situated between limiting conditions defined for amorphous and undamaged silicon.

In contrast with the thermal models of defect annealing, Suski et al. /31/ suggest that the recovery of the B - V complex at high energy (≥ 1 J/cm^2) for the ruby laser (20 ns) is due to the ionization effect (plasma model) because of the high activation energy of the defect (5.6 eV /32/).

The fact that Kachurin /26/ finds only 0.2 µm of melting at 2.5 J/cm^2 is surprissing if we compare this result to that expected in the classical thermal model in which a melt depth greater than 0.5 µm is generally expected. This may mean that the melting threshold and temperature profile is crystalline silicon can be different from those expected /33/. Recently some authors /34, 35/ have included in their thermal model the crystalline quality represented by the probability of diffusion of the photogenerated carriers before their thermalization. So that due to the increase of the diffusion length as a function of the resistivity of the material, the melting threshold can be higher that those reported by the classical thermal model. However this variation of the melting threshold is not sufficiently important to explain the very thin melt region found by Kachurin /26/.



As a conclusion to these first two sections, we can say that the short duration of heating is highly advantageous to the electrical activation of the implanted dopant, offering at the same time a complete absence of macroscopic defects such as dislocations or stacking faults.

Fig. 13 - Unannealed divacancy fractions versus 25 nsec ruby laser energies. Each point was taken on a separate sample. /30/.

However, the pulse heating has a serious drawback in the annealing of point defects in region deeper than that reach by the melting. Then from the practical point of view, nanosecond laser annealing of slightly disordered silicon or the region beyond the amorphized layer should be used in combination with millisecond or continuous low temperature treatment as shown in Fig. 10.

III - PULSED LASER EFFECT IN CRYSTALLINE SILICON

The first observations of damaged role of the pulsed laser have been made on photodiode, phototransistor and solar cells /36, 38/.

In order to analyse the defects created by the laser process alone, we consider in this section the virgin crystalline silicon.

In such material, the primary effect directly observed is the degradation of I - V characteristics /39, 40/ as shown in Fig. 14 a) and b).

These results obtained with ruby laser (20 ns) on N-type silicon demonstrate the responsability of the laser in the creation of trapping and recombination levels near the surface. These recombination centers determine the reverse current of the schottky diode /41, 42/. The experiment of figure 14 (b) shows moreover that the majority of defects are located within the molten region, so that we can confirm that in the case of a P - N junction (in which the space charge region begins near the melting limit) the observed defects are mostly correlated to residual implanted damage. Many defects analysis results have been given in the literature. The electrical parameters of these defects, determined essentially by the DLTS method, are summarized in Table I for N-type silicon irradiated with ruby and Nd : YAG laser.

Concerning the energy levels of the traps detected, the results are quite different from author to author. However, all references agree about the thermal annealing temperature. The high values obtained indicate the stability of the point defects created by the laser process.

Generally the quenching is employed to explain the observed defects. However in the case of pulsed laser, the rate of quenching is more that three or four orders of magnitude shorter than transient used previously. Besides in the quenching model,

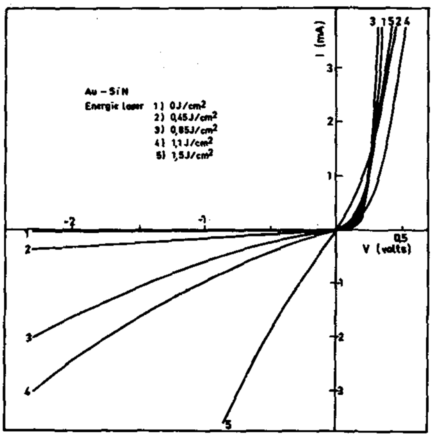


Fig. 14 a) - Influence of laser energy on the I-V characteristics of Au-Si diodes realized on irradiated surfaces /39/.

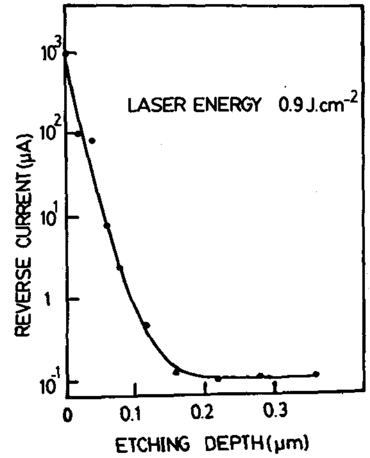


Fig. 14 b) - Change of the average leakage current of Schottky diodes on a Si sample irradiated with a single pulsed laser with etching depth. The damaged layer has a depth comparable to the melting depth of about 0.2 μm. /40/.

the nature of the defects depends strongly on the initial impurity content /45/ such as oxygen, carbon, dopant ...,on the degree of structural imperfection of the material that determines the threshold melting as we have seen in the previous section.

This probably explains the dispersion observed in the energies levels of traps of Table I.

Laser type	Irrad.Energy (J/cm2)	Energies levels $E_c - E_T$ (eV)	Capture cross sect. (cm2)	Thermal anneal. (°C)	REF.
Ruby (20ns)	.9	.25 .32 .49	9 E-16 2 E-16 7 E-16	800	/39/
Ruby (25ns)	1	.41 .53		800	* *
Ruby (30ns)	2.5	.23 .28 .42			/43/
Ruby (50ns)	.9	.41 .51			/44/
YAG (.53μm, 100ns)	2	.41 .53		600	* *
YAG (40ns) 1.06μm and .53μm	14 4.4	.19 .23 .33-.38 .43 .48	5 E-19 5 E-18	550 400 650 650 600	/6/

TABLE I

* * Results unpublished

Other mechanisms should be taken into account in the formation of lattice defects. The high stress gradient (10^{8}°C/cm) and the presence of shock waves has been shown by some authors /46, 47/ to be active.

In P-type silicon, fewer point defect analyses have been made. DLTS analyses performed by Mooney et al. /48/ has shown a level situated at Ev + 0.24 eV. Besides Kimerling et al. /6/ has shown that the irradiation of P-type silicon creates an exponential distribution of the free carriers near the surface as shown in Fig. 15.

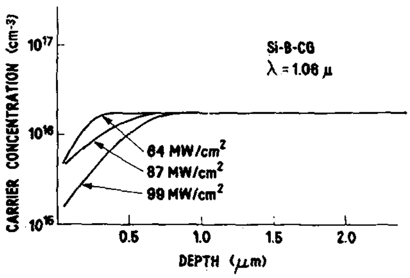


Fig. 15 - Spreading resistance profile of bare, P-type substrates processed in the liquid phase regime (pulse width = 150 ns). The exponential distribution suggests a diffusion process. /6/.

This illustrates the compensating effect created by the presence of minority carrier traps. Using sup-band gap light as an excitation source/ /49/. Mesli et al. have found three levels corresponding to minority carrier traps with large capture cross sections (Fig. 16). One of them (E_c = 0.30 eV) is probably a vacancy-oxygen complex in view of the variation of their concentration in CZ and FZ material. However the deep level (Ec - 0.41 eV) is absent in the CZ substrate. This suggests a competition between Ec - 0.41 eV and Ec - 0.30 eV related to oxygen density.

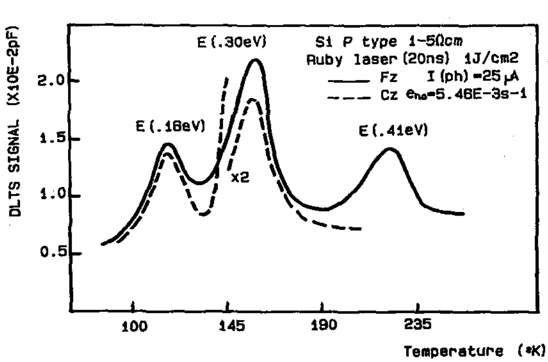


Fig. 16 - Minority defects states spectrum in P-type Schottky diode. The capture cross-sections are respectively σ_n = 2 10^{-14}, 5.7 10^{-15} and 3.5 10^{-15} cm^2.

Analysis of N and P-type silicon has shown that the major observed defects act as electron traps. The role of oxygen in the formation of defects seems be ambiguous. In N-type material no variation in the DLTS peak height versus oxygen density has been observed /6, 43/. But this impurity seems be active in P-type silicon. Moreover these defects exhibit high stability.

If we consider the quenching model where the vacancies generated at high temperature could precipitate during the fast cooling, we suggest the vacancy-oxygen complex and clusters of vacancy like surface defects (Ec = 0.53 eV), divacancies (Ec = 0.41 eV), pentavacancies V^5 (Ec = 0.34 eV) or divacancy-oxygen $V^2 - 0^2$ (Ec - 0.27 eV) as assignments for the observed defects. All these assignments are coherent with the fact that a relative high temperature (≃ 500° C) is needed to remove the observed defects.

CONCLUSION

As a general conclusion on the origin of point defects present after pulsed laser irradiation, it has been shown that essentially a residual tail of implanted defects subsist in a region deeper than the molten layer for P - N junction prepared by ion bombardment with subsequent laser annealing.

In slightly disordered materials, the recovery of defects depends in their nature, so that the annealing of deep lying defects in the crystal is better achieved by longer annealing time (msec to sec) or otherwise needs a post laser thermal treatment. Finally in virgin silicon, stable defects found in the molten layer are mostly correlated to an association of vacancies, which anneals in the range of 500 - 600° C. They are mainly electron traps which can play a compensating role in P-type materials.

REFERENCES

/1/. FOTI G., CAMPASINO S.U., RIMINI E. and VITALI G.. J. Appl. Phys. 49 (1978) 2569.
/2/. CELLER G.K., POATE J.M. and KIMERLING L.C.. Appl. Phys. Lett. 32 (1978) 464.
/3/. NARAYAN I., YOUNG R.T. and WHITE C.W.. J. Appl. Phys. 49 (1978) 3912.
/4/. CULLIS A.G., POATE J.M. and CELLER G.K.. MRS Symposium Proceedings Laser Solid Interaction and Laser Processing (Boston USA 1978). FERRIS S.D., LEAMY M.L. and POATE J.M. eds (Am. Inst. Phys. N.Y. 1979) 311.
/5/. CULLIS A.G.. MRS Symposium Proceedings Vol. 2 Defects in Semi-conductors. NARAYAN J., TAN F.Y. eds (1981) 393.
/6/. KIMERLING L.C. and BENTON J.L.. MRS Symposium Proceedings Laser and Electron beam processing of materials (1979), WHITE C.W., PEERCY P.S. eds (Ac. Press 1980) 385.
/7/. MESLI A., MULLER J.C., SALLES D. and SIFFERT P.. Appl. Phys. Lett. 39 (1981) 159.
/8/. BENTON J.L., KIMERLING L.C., MILLER G.L., ROBINSON D.A.H. and CELLER G.K. MRS Symposium Proceedings Laser Solid Interaction and Laser Processing (Boston USA 1978) 543.
/9/. MILLER G.L., BENTON J.L., KIMERLING L.C., ROBINSON D.A.H. and RODGERS J.W.. Semicond. Characterization Technics (Electr. Chem. Society Princeton 1978) 502.
/10/. JOHNSON N.M., GOLD P.B., LIETOILA A. and GIBBONS J.F.. MRS Symposium Proceedings Laser Solid Interaction and Laser Processing (Boston USA 1978) 550.
/11/. WANG V.L., LIU Y.S., KIRKPATRICK C.G. and POSSIN G.E.. MRS Symposium Proceedings Laser Solid Interaction and Laser Processing (Boston USA 1978) 569.
/12/. SKOLNICK M.S., CULLIS A.G. and WEBBER H.C.. Appl. Phys. Lett. 38 (1981) 464.
/13/. BROWER K.L., PEERCY P.S.. MRS Symposium Proceedings Laser and Electron beam processing of materials (1979) 441.
/14/. BLOOD P., DEARNALEY G. and WILKINS M.A.. Rad. Eff. 21 (1974) 245.
/15/. BLOOD P., DEARNALEY G. and WILKINS M.A.. J. Appl. Phys. 45 (1974) 5123.
/16/. MESLI A., GOLTZENE A., MULLER J.C., MEYER B, SCHWAB C. and SIFFERT P.. MRS Symposium Proceedings Laser and Electron beam Interaction with Solids (Boston USA 1981). APPLETON B.R. and CELLER G.K. eds, 349.
/17/. SERVIDORI M., ZANI A. and GARULLI . Phys. Stat. Sol. (a) 70 (1982) 691.
/18/. SASAKI Y., TSUJIMOTO K., SUSUKI T., ITOH K. and MITSUISHI T.. Defects and Rad. Eff. in Semicond. Proceedings (Oiso, Japan, 1980). Inst. Phys. Conf. No. 59 (1980) 497.
/19/. BELL R.O., TOULEMONDE M. and SIFFERT P.. Appl. Phys. 19 (1979) 313.
/20/. NAKASHIMA H., SHIRAKI Y. and MIYAO M.. J. Appl. Phys. 50 (1979) 5966.
/21/. YOUNG R.T., WOOD R.F., CHRISTIE W.M. and JELLISON Jr. G.E.. Appl. Phys. Lett. 39 (1981) 313.
/22/. ZIGNANI F., GALLONI R., PEDULLI L., BENTINI G.G., SERVIDORI M., CEMBALI F. and DESALVO A.. Photovoltoic Solar Energy Conf. Berlin (W.G.) (1979) REIDEL D. ed. 213.
/23/. MULLER J.C. and SIFFERT P.. Rad. Effects 63 (1982) 81.
/24/. PRUSSIN S., VON DER OHE W.. J. Appl. Phys. 51 (1980) 3853.
/25/. KACHURIN G.A., NIDAEV E.V. and DANYUSTIKINA N.V.. Sov. Phys. Semicond. 14 (1980) 386.
/26/. KACHURIN G.A., NIDAEV E.V. and POPOV A.I.. Sov. Phys. Semicond. 16 (1982) 13.
/27/. KIMERLING L.C., DE ANGELIS H.M. and CARNES C.P.. Phys. Rev. B 3 (1971) 427.
/28/ KIMERLING L.C., DE ANGELIS H.M. and DIEBOLD J.W.. Solid Stat. Communication 16 (1975) 171.

/29/. CHENG L.J., CORELLI J.C., CORBETT J.W. and WATKINS G.D.. Phys. Rev. 152 (1966) 761.
/30/. STEIN H.J., KNAPP J.A. and PEERCY P.S.. MRS Symposium Proceedings Laser and Electron beam Interaction with Solids (Boston USA 1981). APPLETON B.R. and CELLER G.K. eds, 349.
/31/. SUSKI J.J., RZEWOSKI H., KRYNICKI J. and GROTZSCHEL R.. Defects and Rad. Eff. in Semicond. Proceedings (Oiso, Japan, 1980). Inst. Phys. Conf. No. 59 (1980) 485.
/32/. RZEWUSKI H. and KRYNICKI J.. Rad. Effects 39 (1978) 123.
/33/. JASTRZEBSKI L., BELL A.E., WU P., ZANZUCCHI P.J.. J. Appl. Phys. 52 (1981) 4276.
/34/. JAROSLOWE and WILCOX Z.. J. Appl. Phys. 51 (1980) 2866.
/35/. KIM DAE.M., KONG D.L.. IEEE J. of Quantum Elect. QE 18 (1982) 224.
/36/. KRUER M., ALLEN R., ESTEROWITZ L., BARTOLI F.. Optical and Quantum Electronics 8 (1976) 453.
/37/. MATSURKA Y. and USEMI A.. Appl. Phys. Lett. 25 (1974) 574.
/38/. GIULIANI J.F. and MARQUARDT C.L.. J. Appl. Phys. 45 (1974) 4993.
/39/. BUTTUNG E.. Thesis University Strasbourg (France) (1981).
/40/. FAN Z.K., HO V.Q. and SUGONO T..Appl. Phys. Lett. 40 (1982) 418.
/41/. GROVE A.S..Physique et Technologie des Dispositifs à Semi-conducteurs. Ed. DUNOD (1971) 173.
/42/. SZE S.M.. Physics of Semiconductor Devices. WILEY J. and SONS, N.Y. (1969) 102.
/43/. KACHURIN G.A., NIDAEV E.V. and POPOV A.J.. Sov. Phys. Semicond. 16 (1982) 688.
/44/. LYSENKO K.S., NAZOROV A.N., LOKSHIN M. and KASCHIEVA S.B.. Sov. Phys. Semicond. 11 (1977) 1327.
/45/. MASHOVETS T.V.. Sov. Phys. Semicond. 16 (1982) 1.
/46/. NIKIFOROV YU. N., YANUSHKEVICH V.A.. Sov. Phys. Semicond. 14 (1980) 314.
/47/. IVANOV L.I., NIKIFOROV YU. N. and YANUSHKEVICH V.A.. Sov. Phys. JETP 40 (1974) 75.
/48/. MOONEY P.M., YOUNG R.T., KARINS J., LEE Y.H. and CORBETT J.W.. Phys. Stat. Sol. (a) 48 (1978) K31.
/49/. HAMILTON B. and PEAKER A.R.. J. Appl. Phys. 50 (1979) 6373.